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A STUDY ON THE Cr(VI) REMOVAL FROM AQUEOUS SOLUTIONS BY STEEL WOOL

A. Özer, H. S. Altundoğan,* M. Erdem and F. Tümen

Department of Chemical Engineering, Fırat University, 23279 Elazığ, Turkey

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Abstract

The reduction of Cr(VI) by steel wool and the precipitation of reduced chromium by $CaCO_3$ powder and NaOH solution were investigated in continuous and batch systems, respectively. The effects of acid and initial Cr(VI) concentrations, volumetric rate and temperature of solution on Cr(VI) reduction were studied. The results showed that the reduction of Cr(VI), to a large extent, depended on, and increased with, acid concentration. The Cr(III) and iron ions in the reduced solution were completely precipitated by using NaOH solution at appropriate alkaline conditions. It was concluded that $CaCO_3$ powder could be used as a cheap precipitant for Cr(III) ions. But the iron ions in the reduced solution could not be fully removed by using this precipitant. © *1997 Elsevier Science Ltd*

Keywords: Steel wool, hexavalent chromium, reduction, precipitation.

INTRODUCTION

Chromium is a priority metal pollutant introduced into natural waters from many industrial processes including leather tanning, textile, electroplating, metal cleaning, wood preservation and alloy preparation. Chromium is found in two stable forms in aquatic systems, Cr(VI) and Cr(III) (Dean *et al.*, 1972). The former is well known for its toxicity and is believed to be carcinogenic (Sittig, 1973; Moore and Ramamoorthy, 1983). Cr(III) may also have toxic effects, but its concentration is usually well below water quality standards due to the low solubility of chromium hydroxide in the pH range of natural waters. The permissible limit of chromium present in drinking water is 0.05 mg litre^{-1} (Förstner and Wittmann, 1981; Hammer, 1986). For that reason, chromium containing wastewaters must be treated to lower the Cr(VI) concentration to allowable limits before discharging into the environment.

The conventional method of treating wastewater containing Cr(VI) includes its reduction to the trivalent state followed by alkaline precipitation as chromium hydroxide. The reducing agents commonly used for chromium wastes are sulphur dioxide, sodium sulphites and ferrous sulphate (Patterson, 1975; Bridgwater and Mumford, 1979; Sittig, 1973). Besides these, the utilization of various reductants containing ferrous iron compounds are described in literature (Lancy, 1966; Eary and Rai, 1988; Anderson *et al.*, 1984). The reduction of hexavalent chromium by ferrous iron compounds is based on the reducing ability of ferrous ions produced from soluble ferrous salts. Ferrous sulphate is the most commonly used reagent for reduction of hexavalent chromium. In order to obtain a complete reaction, however, an excess dosage of 2–2.5× of the theoretical amount of ferrous sulphate must be used (Eckenfelder, 1989; Lanouette, 1977). The use of ferrous sulphate as reducing agent has the disadvantage that a large amount of $Fe(OH)_3$ is formed at the stage of alkaline precipitation. In addition, this process introduces excessive amount of sulphate ions as a contaminant into wastewater.

In this study, the use of steel wool as an alternate agent for the reduction of Cr(VI) in a continuous system was examined. The optimum conditions were determined by studying acid and initial Cr(VI) concentrations, volumetric rate of solution and temperature. After having obtained optimum conditions for reduction, removal of Cr(III) and iron ions by alkaline precipitation in the treated solution was investigated.

MATERIALS AND METHODS

Materials

Reducing material used in the experiments is a fine fibrous steel wool which is widely used for surface cleaning purposes. The diameter of steel wool fibers ranges from 30 to 300 μm. Chemical analysis showed that it mainly consisted of iron and was free from chromium.

Feed solutions at different concentrations were prepared by dissolving $K_2Cr_2O_7$ in distilled water. Sulphuric acid was used for adjusting pH of the feed solution. NaOH solution and $CaCO_3$ powder were used as precipitation agents. All chemicals used were of analytical reagent grade.

*To whom correspondence should be addressed. Fax: 090 424 2181907.

Apparatus

Reduction experiments were conducted by using a jacketed glass column (i.d. = 3.5 cm, ht = 20 cm) with a porous plate (Por. No: 0) at the bottom. The system was equipped with a temperature controlled circulatory water bath, two heat exchangers, an air pump and a reservoir bottle. A schematic diagram of the system is given in Fig. 1.

Experimental procedure

One gram of steel wool prepared in cylindrical shape (8 cm ht) was placed on the porous plate in the column. The top of the steel wool was covered with a piece of glass wool. To keep the temperature of the solution constant, water taken from a temperature controlled water bath was circulated within the preheaters and the jacket. When the temperature of the bath became constant, the feed solution was allowed to pass upward through the steel wool bed. Water saturated air in a constant flow rate (250 $cm^3 min^{-1}$) was sent from the bottom of the column by means of an air-pump to obtain a homogenous mixing. The steady volumetric rate was obtained by keeping the same level, at the outlet, of reduced solution, about 10 cm above the porous plate, with the inlet of feed solution from reservoir (the dotted line in Fig. 1 shows this level). The volumetric rate was set by a valve fitted onto the feeding line. During the reacting period, the effluent leaving the column at constant rate was collected in 100 ml fractions, and each was analysed for Cr(VI), total chromium and iron ions. This procedure was continued until Cr(VI) concentration in the effluent was raised to nearly that of feed solution.

After optimum conditions were determined for reduction, the solution containing 500 mg Cr(VI) per litre (H_2SO_4 concentration 0.05 M) was passed through the column packed with one gram of steel wool at 25°C, until Cr(VI) was detected in effluent. The effluent was collected in a reservoir and its Cr(III) and iron concentrations were determined. This reduced solution was subjected to precipitation tests. Precipitation of Cr(III) and iron were carried out by shaking 50 ml of the solution with varying amounts of $CaCO_3$. In addition, a series of precipitation experiments were performed by adding varying amounts of NaOH solution (1.0 M) to 50 ml of reduced solution. The final volume of mixtures was recorded. The mixture was shaken at 25°C for 1 h in a temperature controlled water bath. After the shaking period, the reaction mixture was filtered through a S&S 589 filter paper. Supernatants were analysed for chromium and iron. The removal yield was calculated from the concentration difference.

Methods of analysis

The analysis of Cr(VI) was carried out colorimetrically with the 1,5-diphenil carbazide method (APHA, 1975) by spectrophotometer (Bausch & Lomb, Spectronic 20). The concentration of total chromium and iron were determined (ASTM, 1984) by using a Perkin-Elmer 370 model atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Reduction experiments

The reduction of $Cr_2O_7^{2-}$ by steel wool occurs in acidic aqueous solutions, and the reduction mechanism can be described by the following reactions.

$$2Cr_2O^{2-}_{7(aq)} + 6Fe^0_{(s)} + 28\ H^+_{(aq)} \rightarrow 4Cr^{3+}_{(aq)} + 6Fe^{2+}_{(aq)} + 14H_2O \quad (1)$$

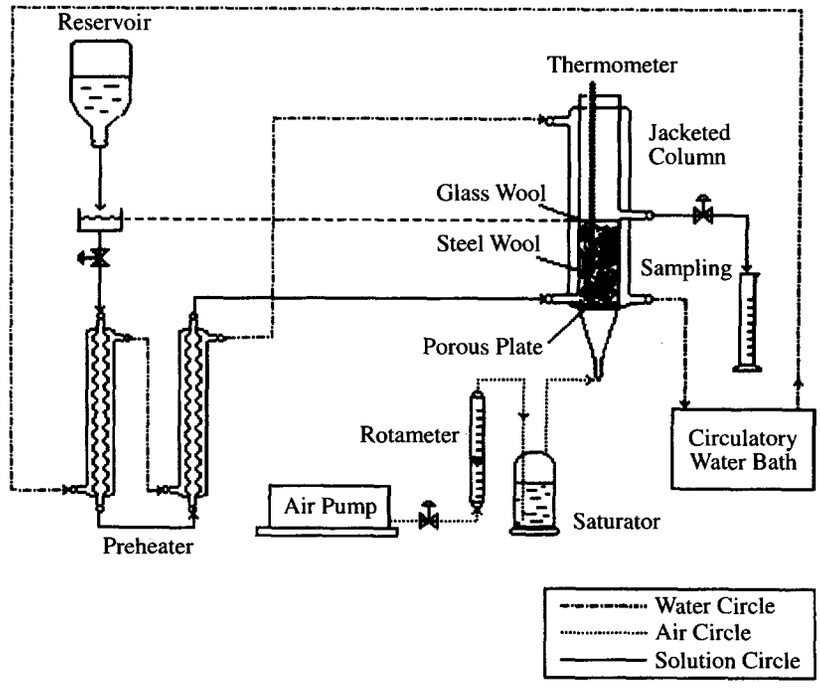

Fig. 1. Schematic diagram of experimental apparatus.

$$Cr_2O_{7(aq)}^{2-} + 6Fe_{(aq)}^{2+} + 14\ H_{(aq)}^{+} \rightarrow 2Cr_{(aq)}^{3+} + 6Fe_{(aq)}^{3+} + 7H_2O \quad (2)$$

The two equations can be added together to yield eqn (3) which is a net reaction for the process.

$$Cr_2O_{7(aq)}^{2-} + 2Fe_{(s)}^{0} + 14\ H_{(aq)}^{+} \rightarrow 2Cr_{(aq)}^{3+} + 2Fe_{(aq)}^{3+} + 7H_2O \quad (3)$$

The stoichiometry of this reaction requires 14 mol hydrogen ions, which corresponds 7 mol of H_2SO_4 for each 2 mol of Cr(VI). It is obvious that the reduction efficiency is highly dependent on acid concentration. For that reason, the first section of this work was performed with different amounts of acid (1.0, 1.5 and 2.0 stoichiometric amounts of H_2SO_4) and a 10 ml min^{-1} volumetric rate of solution for a Cr(VI) concentration of 500 mg litre^{-1}. The results of these experiments are shown in Fig. 2. In the experiments carried out with one stoichiometric amount of acid with respect to 500 mg Cr(VI) per litre of solution, the Cr(VI) in the 800 ml of solution was completely reduced to Cr(III). Total iron in this solution was found to be 533.9 mg [667.4 mg litre^{-1}(Fe)]. With the same conditions, but increasing of acid concentration to 1.5 and 2.0× the stoichiometric ratio, the volume of treated solution (not containing hexavalent chromium) increased to 1000 and 1100 ml. In these cases, total iron concentrations in the solutions were determined as 689 and 720 mg litre^{-1}, respectively. The molar ratios of (dissolved iron)/(reduced chromium) were found as 1.24, 1.28 and 1.34 for 1.0, 1.5 and 2.0 stoichiometric acid content, respectively. However, eqn (3) requires 1 mol iron for each mol chromium reduced. As seen from the above figures, the solubilized iron concentration in the treated solution increases as the initial pH of the solution is decreased. However, the reduction of Cr(VI) occurs nonstoichiometrically relative to dissolved iron in the treated solution. Steel wool is readily solubilized by reacting with dilute acid to form ferrous ions and it is possible that the Fe(II) ions may form in the first oxidation step of steel wool (eqn (4)).

$$Fe_{(s)}^{0} + 2H_{(aq)}^{+} \rightarrow Fe_{(aq)}^{2+} + H_{2(g)} \quad (4)$$

Conversely, ferrous ions can be converted to ferric ions by the dissolved oxygen provided by aeration to obtain a homogenous mixing. Oxidation of Fe(II) by dissolved oxygen has been reported to be a function of pH (Eary and Rai, 1988). Oxidation reaction can be described as following.

$$Fe_{(aq)}^{2+} + 1/2\ O_{2(dissolved)} + 2H_{(aq)}^{+} \rightarrow Fe_{(aq)}^{3+} + H_2O \quad (5)$$

As a result, the solubilizing rate of steel wool is directly dependent on the concentration of acid and dissolved oxygen. The higher acid concentration, the more iron is dissolved in the treated solution. The dissolved iron and excess acid in the solution can be considered as contaminants which must be removed in the final step. Hence, both to treat the maximum amount of solution and to reduce the amount of solubilized iron, subsequent experiments were carried out with 1.5× the stoichiometric acid.

The influence of the volumetric rate of feed solution on reduction of Cr(VI) is shown in Fig. 3. These experiments were performed at volumetric rates of 20 and 40 ml min^{-1}. As seen from Fig. 3, volumetric rate has no significant effect on the reduction efficiency. However, the amount of solubilized iron in the treated solution decreased with increasing volumetric rate of solution. In the experiments performed with 20 and 40 ml min^{-1} volumetric rates, Cr(VI) was detected at the 11th and 10th period, respectively. This situation may be attributed to the decrease of contact time of solution with steel wool as a result of the increasing volumetric rate. While more solution is treated at volumetric rate of 40 ml min^{-1} compared to that of 20 ml min^{-1}, it is difficult to keep the volumetric rate at 40 ml min^{-1} by manual control, hence, 20 ml min^{-1} was selected for further runs.

Figure 4 shows the results of studies carried out at 40, 50 and 60°C. It can be seen that the temperature of solution has no effect on the reduction of Cr(VI) when the amount of the treated solution is considered. However, the concentration of iron in treated solutions shows an increasing trend with the temperature of solution. For example, dissolved iron concentration in the treated solutions at the same period are about 620, 670

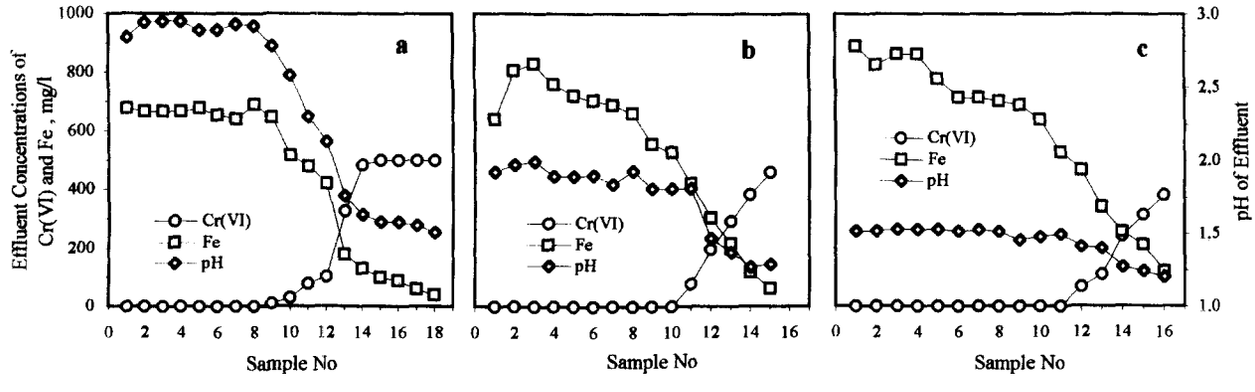

Fig. 2. Effect of acid concentration on the Cr(VI) reduction. (a) 1.0, (b) 1.5 and (c) 2.0× of stoichiometric amount of H_2SO_4 (initial Cr(VI) conc., 500 mg litre^{-1}; volumetric rate, 10 ml min^{-1}; temperature, 25°C).

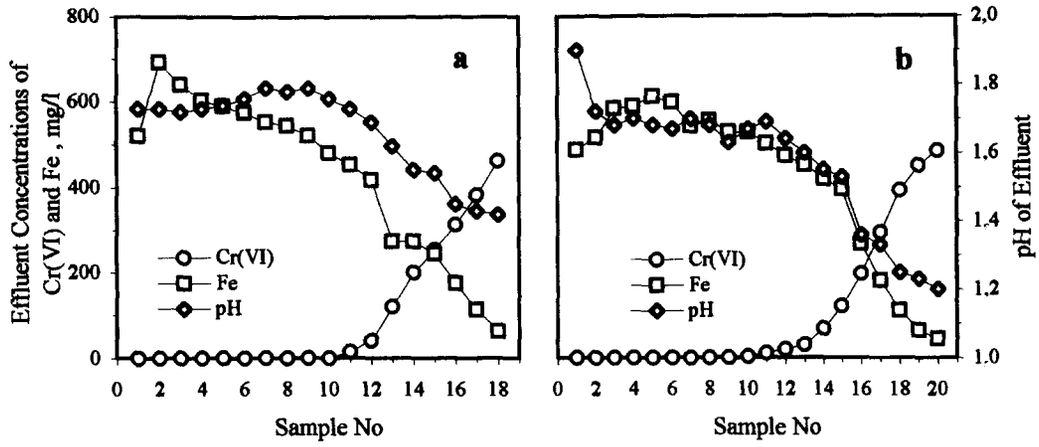

Fig. 3. Effect of volumetric rate on the Cr(VI) reduction. (a) 20 and (b) 40 ml min^{-1} (initial Cr(VI) conc., 500 mg $litre^{-1}$; 1.5 stoichiometric H_2SO_4, temperature, 25°C).

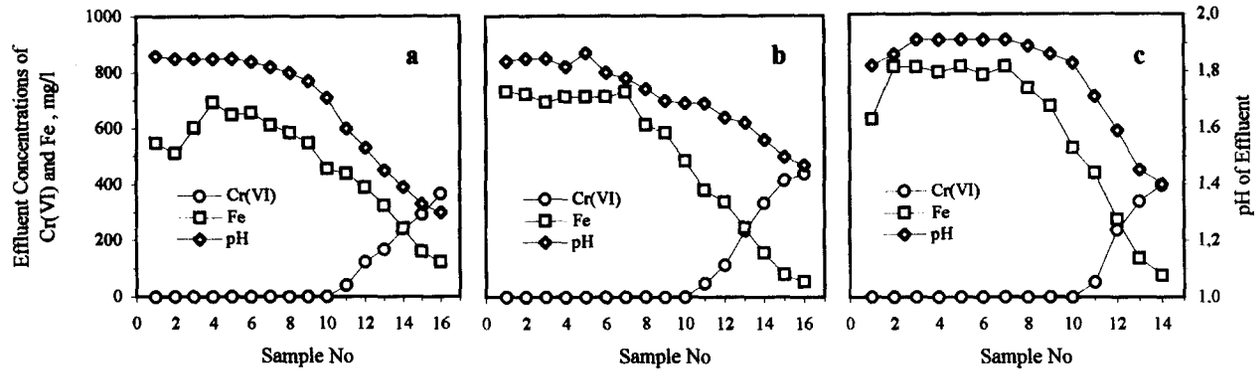

Fig. 4. Effect of temperature on the Cr(VI) reduction. (a) 40, (b) 50 and (c) 60°C (initial Cr(VI) conc., 500 mg $litre^{-1}$; 1.5 stoichiometric H_2SO_4; volumetric rate, 20 ml min^{-1}).

and 742 mg $litre^{-1}$ at 40, 50 and 60°C, respectively. On the other hand, the amount of reduced chromium is nearly constant for these three temperatures. Because the cost of the process will increase with temperature, the lower temperature may be considered advantageous.

The effect of initial Cr(VI) concentration on the reduction process is shown in Fig. 5. With increase of the initial Cr(VI) concentration from 250 to 750 mg $litre^{-1}$ the amount of treated solution decreased from 1800 to 700 ml. The amount of treated solution for 500 mg $litre^{-1}$ initial Cr(VI) concentration is 1000 ml (Fig. 2(b)). Total iron values determined in the treated solutions are 558, 689 and 569 mg and molar ratios of dissolved iron to reduced chromium were found to be 1.15, 1.28 and 1.01 for initial Cr(VI) concentrations of 250, 500 and 750 mg $litre^{-1}$, respectively. These ratios show that there is no regular relationship between dissolved iron and reduced chromium. However, it is clear that the higher initial concentration of Cr(VI), the smaller the amount of solution treated. In the experiment carried out with an initial concentration of 1000 mg $litre^{-1}$ Cr(VI) was determined as 31.6 mg in the first 100 ml effluent. Because the aim is to reduce Cr(VI) completely, the initial Cr(VI) concentrations higher

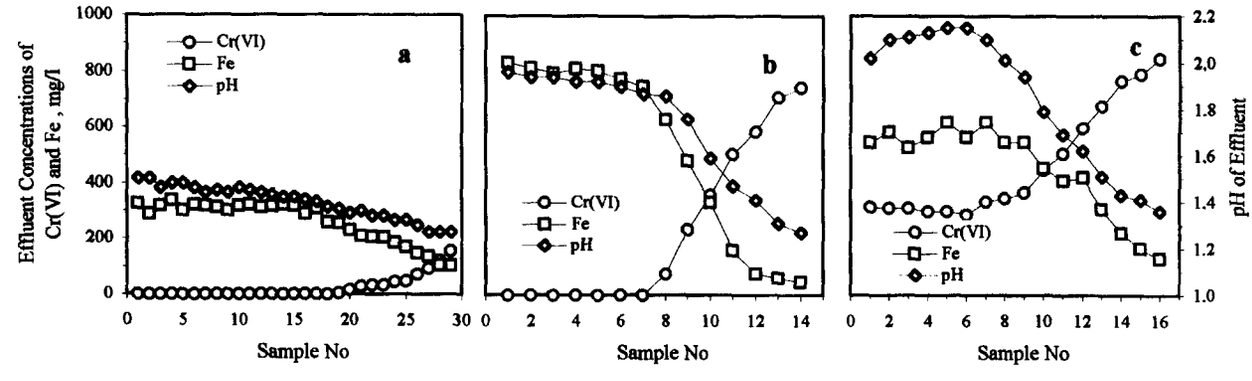

Fig. 5. Effect of initial Cr(VI) concentration on the reduction process. (a) 250, (b) 750 and (c) 1000 mg Cr(VI)$litre^{-1}$ (1.5 stoichiometric H_2SO_4; temperature, 25°C; volumetric rate, 20 ml min^{-1}).

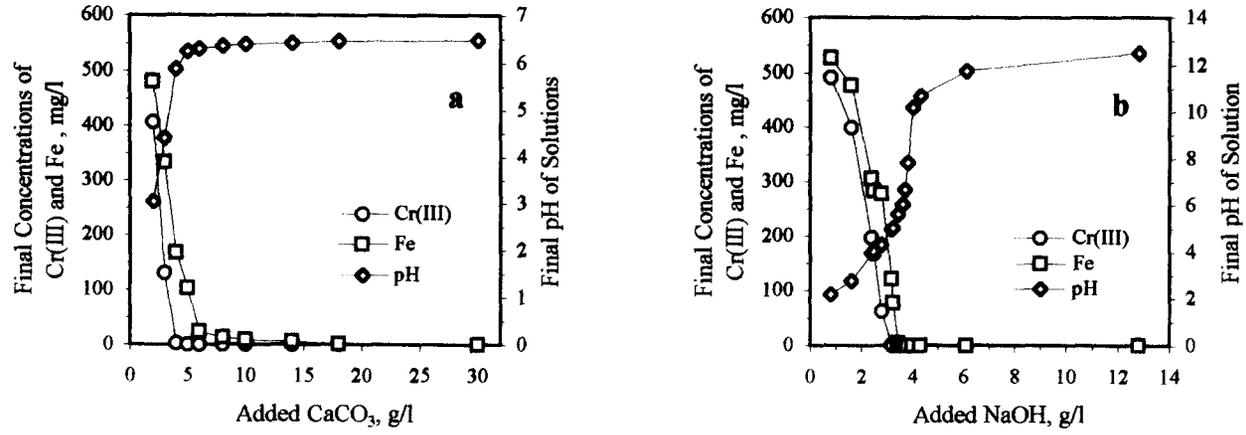

Fig. 6. Results of precipitation experiments obtained by $CaCO_3$ (a) and NaOH solution (b) (Cr(III) conc., 494 mg litre^{-1}; iron conc., 572 mg litre^{-1}; initial pH 1.74; shaking time, 30 min; temperature, 25°C).

than 750 mg litre^{-1} are not suitable for the conditions applied in this work. If the retention time of Cr(VI) solution in the bed, the amount of steel wool and acidity of solution are increased, solutions with higher Cr(VI) concentrations may be treated by this process, but then the optimum conditions must be re-examined.

Precipitation experiments

The concentration of Cr(III) and total iron in the solution subjected to precipitation tests were 494 and 572 mg litre^{-1}, respectively. The initial pH of the solution was 1.74. The precipitation experiments were carried out by adding $CaCO_3$ powder and NaOH solution to the reduced solution. The results of these experiments are shown in Fig. 6. The precipitation mechanism of Cr(III) and iron ions by $CaCO_{3(s)}$ is based on the neutralization of excess acid in the reduced solutions (Özer *et al.*, 1993). This mechanism can be described as following.

$$CaCO_{3(s)} + 2H^{+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O \quad (6)$$

The precipitation yield of Cr(III) and iron ions depends on the pH of the mixture. While the pH of the mixture increased by adding $CaCO_{3(s)}$ or NaOH solution, the concentration of Cr(III) and iron in the supernatant decreased. The Cr(III) ions in 50 ml of reduced solution were completely precipitated with 0.25 g $CaCO_3$ (Fig. 6(a)). Under these conditions, the final iron concentration in the supernatant was about 103 mg litre^{-1}. Since $CaCO_3$ has a low cost, it appears to be a good precipitation agent for the Cr(III) ions. The amount of $CaCO_3$ added was increased to lower the concentration of iron ions in the supernatant. By using 30 g litre^{-1} $CaCO_3$, the final iron concentration could be reduced to 0.17 mg litre^{-1}, corresponding to about 99.99% iron removal.

The precipitation efficiency of Cr(III) was increased in the experiments carried out by adding NaOH solution. Figure 6(b) shows that all the Cr(III) ions are precipitated in the pH range of 6.03–7.83. In strongly alkaline conditions, Cr(III) ions could not be completely removed from the solution, probably due to the amphoteric characteristic of Cr(III). In the NaOH-precipitation experiments, the iron ions in the reduced solution were completely removed at pH values above 7.83. The iron ions could be more effectively precipitated by using NaOH solution than with $CaCO_{3(s)}$.

CONCLUSIONS

The experimental results presented here indicate that the Cr(VI) in aqueous solution can be effectively reduced by using steel wool. This reduction process may be readily used in the treatment of electroplating wastewater containing high amounts of Cr(VI) ions and acid. Such wastewaters do not require additional acid for pH adjusting. This situation can be considered as an advantage for the reduction process. Cr(III) and iron ions can be removed by treating the reduced solutions with NaOH solution or $CaCO_3$. In all cases, the use of $CaCO_3$ in the former step will reduce the cost of the precipitation process.

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